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(57) Abstract

In an improved method of manufacturing biodegradable plastics material, a polyhydroxylated polymer such as polyvinylalcohol and polyvinylalcohol/polyvinylacetate copolymer (PVA/PVAc) is mixed with a plasticiser and a stabiliser under conditions of applied physical force and temperature which enable the polymer to be worked without any significant degradation. The stabiliser may be any surface active agent, dispersing agent and/or mould lubricant, except stearamide or stearic acid when used at a mixing temperature of between 160 and 140 °C. A blend of stabilisers may be used. The stabiliser enhances the action of the plasticiser and maintains the stability of the resultant compound enabling it to be reproducibly thermoplastically processed and to yield products with minimal discoloration which can be effectively biodegraded. Compounded material with a melt flow index in the range of 0.2–375 g/10 min. at 190 °C using 21.6 Kg ISO 1133 method can be produced at temperatures in the range of 140 °C to 205 °C.

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IMPROVED BIODEGRADABLE PLASTICS MATERIAL AND A METHOD FOR ITS MANUFACTURE

The present invention relates to a biodegradable plastic compound for use in thermoplastic applications and to its method of manufacture, and in particular to biodegradable polymers including, but not limited to, polyvinylalcohol (PVA) and polyvinylalcohol/ polyvinylacetate copolymer, (PVA/PVAc).

PVA and PVA/PVAc copolymers are known biodegradable materials. PVA and PVA/PVAc (of greater than 85% PVA) are soluble in warm and hot water. PVA/PVAc (of less than 85% PVA content) is readily soluble in water at room temperature. Post dissolution these materials will bio-degrade on exposure to bacteria present in the environment. These polymers and their part degradation and degradation products are non-toxic and pose no risk of bio-accumulation or long term hazard to the environment.

The applications of PVA and PVA/PVAc in thermoplastics have been limited by degradation which can occur on thermal processing. The susceptibility of PVA to thermal damage has long since been known. Work by Brown in 1952, (Rubber Age, Nov. 1952, p211-214) sought to improve the processability of PVA by simple cast plasticisation with glycerol, sorbitol and other similar materials under pressure at 140°C.

US-A-1,040,506 (Monsanto) discloses a process of manufacturing PVA film at 196-218°C, using mould lubricants as auxiliaries in amounts from 0.2-2%.

US-A-3,997,489 (Du Pont) discloses the improvement of melt flow index (MFI) of plasticised PVA by the addition of 0.5-5 % by weight of wax or waxy materials and 0.5-5% of polyethylene polymer or copolymers which enabled thermoplastic processing at 205-240°C. MFI data was determined at 210°C and 230°C. Also, US-A-5,206,278 discloses extrudable compositions of plasticised PVA co-compounded with 5-95 weight % of polyethylene oxide (PEO) or PEO copolymers of average molecular weight 100,000-500,000. US-A-5,349,000 (Air products) discloses plasticised PVA co-compounded with

8-25 weight % polyester-polyether block-copolymers, the compound being processed at 200°C.

The Hoechst process described by Zimmermann and Harreus in EP-A-0004587 and US-A-4,323,492, (Zimmermann et al) has claimed the improve plasticisation of PVA by specific particle size control of materials blended in a force action mixer prior to compounding or extrusion. The Hoechst process for the preparation of plasticised PVA film describing the aforementioned plasticisation process is further detailed by Harreus et al, Hoechst Resins Special Print 'Plastics films formed from polyvinyl alcohol' and discloses desired extrusion barrel temperatures of 215-225°C, die extrusion temperatures of 165-195°C, and operating pressures of 150-200 bar for the preparation of cold water soluble film. The PVA Plasticiser blend is described as 'not a free flowing process' with the material described as 'rubber elastic' in behaviour. Additional disclosure in Mowiol - Polyvinyl Alcohol, Hoechst Aktiendeschaft (1991) indicates die extrusion temperatures from 220-150°C depending upon grade of Mowiol (PVA).

Further disclosures by Zimmerman et al in US-A-4,542,178 encompass co-compounded plasticised and unplasticised PVA, optionally with various starch, cellulose, gelatine or vinyl based fillers. Also Zimmermann et al in US-A-4,656,216/EP-A-0155606 have claimed a film of co-compounded PVA with N-vinyl-N-methylamide, which will retain its water dissolution characteristics on storage with acidic chemicals which would otherwise so degrade water soluble PVA as to render it insoluble. The material is processed at 200°C and extruded at 170°C at the die.

US-A-4,469,837 (Cattaneo) describes a compound based on PVA, and polyol plasticisers such as Glycerol, Mannitol and Pentaerythriol with working extrusion temperatures from 190-220°C. Also, US-A- 4,529,666 discloses similar materials based on one or more 1,4-monoanhydrohexitols and/or one or more 1,4- 3,6-dianhydrohexitols, such as mono and di anhydro-sorbitols and mannitols. Plasticisation is carried out at 170-200°C and materials die extruded at 210-230°C. Similarly, EP-A-0635545-A2 (Air Products) describes a process based on PVA, Glycerol and Pentaerythriol compounding at 195-225°C. This

disclosure claims the addition of small amounts of mineral acids will improve the stability of PVA.

US-A-3,886,112 (Watson and Pucknat) discloses the working of plasticised PVA with 65-98 weight % water and 0.5-5% borate salts. US-A- 5,322,866 discloses a process whereby PVA is co-compounded with starch and 13% w/w water and extruded wet (or semi-dry in the patent terminology), the product necessitating air curing to 5% water before use. Similarly WO93/09171/US-A-5,462,981 (Bastioli et al) discloses a process for the preparation of compound from PVA, plasticisers, starch, 0-7% urea and 5-40% water.

Irish Patent No. S71912/WO 97/09379 discloses that PVA/PVAc copolymer comprising 70-85% PVA and 30-15% PVA with molecular weights in the range 20,000 to 90,000 can be more efficiently plasticised by the addition of 3-15% weight equivalent glycerol with the aid of 4-6% weight equivalent of stearamide or stearic acid salts as a 'stabiliser'. The mixing of components is carried out at 106-140°C and the material processed at 195-225°C into thermoplastic materials.

The present invention seeks to provide an improved method of manufacturing an article or material using biodegradable polymers such as PVA/PVAc and to improved, biodegradable articles prepared using the method.

Accordingly, the present invention provides a method of manufacturing a homogeneous biodegradable plastics compound, comprising mixing a polyhydroxylated polymer or copolymer with a plasticiser or a blend of plasticisers and a stabiliser or a blend of stabilisers, the stabiliser or blend thereof comprising a surface active agent, dispersing aid and/or mould lubricant and thermoplastically processing the mixture at 120°C to 205°C, the thermoplastic processing including compounding the mixture at a temperature in the range of 140°C to 205°C, the resulting compound having a melt flow index of 0.2 to 375 g/10 minutes using 21.6Kg at 190°C (ISO 1133 method), the plasticiser and stabiliser or blends thereof rendering the mixture stable to thermoplastic processing, with the proviso that the stabiliser does not comprise stearamide or stearic acid salt when used singly as the

stabiliser at a mixing temperature of 106°C to 140°C with polyvinylalcohol or polyvinylalcohol/ polyvinylacetate copolymer.

The compounding temperature may be in the range of 140°C to 185°C in which case the biodegradability of the resulting compound is identical to that of the uncompounded mixture of its components.

In the case where the compounding temperature is in the range of 185°C to 205°C, the biodegradability of the resulting compound is reduced by not more than 30% of that of the uncompounded mixture of its components.

The polymer or copolymer may comprise polyvinylalcohol or polyvinylalcohol/ polyvinylacetate copolymer or a co-compound thereof selected from polyethylene, polystyrene, polyhydroxy butyrate, polyhydroxyvalerate, polycaprolactone or any polyhydroxylated polymer or any thermoplastically processable polymer. Alternatively, the polymer or copolymer may comprise any polyhydroxylated polymer.

Conveniently, the blend of stabilisers acts as a super-plasticiser and is used to enhance the effectiveness of the plasticiser by rendering the molten plastic more fluid and easier to process than can be achieved using a single stabiliser. The plasticiser may be selected from any low-volatile or low melting alcohol, ester or ether, or any bi- or tri-functional alcohol, ester or ether or any combination thereof. The plasticiser preferably comprises any material selected from :-

(1) Glycerol, propylene glycol, 1,3-propanediol, ethylene glycol; or

(2) any mono-, di- or tri- (C_1 to C_{10}) carboxylic acid esters of materials listed (1) above; or

(3) citric acid (C_1 to C_4) alcohol tri-esters or mixed tri-esters or glycol esters or (C_1-C_4) acid esters thereof; or

(4) tartaric acid (C_1 to C_4) alcohol di-esters or mixed di-esters or glycol esters; or

(5) lactic acid (C_1 to C_4) alcohol esters, ethylene or propylene glycol esters; or

(6) malic acid (C_1 to C_4) alcohol di-esters or mixed di-esters or glycol esters; or

(7) glyceric acid (C_1 to C_4) alcohol esters or ethylene glycol ester; or

(8) any (C_1 to C_4) ether, glycol ether or mixed ether of materials listed (1) to (7) above; or

(9) any (C_1 to C_4) acetal or ketal derivative of materials listed (1) to (7) above; or

(10) any vegetable base oils including soya oil or corn oil; or

(11) any (C_1 to C_{10}) mono-, di- or tri- ester of adipic acid, azelaic acid, phthalic acid or trimellitic acid;

or any combination of (1) to (11) above

and the stabiliser comprises any material selected from:-

(12) any (C_4 to C_{36}) mono- or di-carboxylic acid; or

(13) any primary, secondary or tertiary amide or diamide of (12) above; or

(14) any inorganic or organic salt of (12) above; or

(15) any mono-, di- or tri glycerol ester or mixed glycerol ester of (12) above; or

(16) any ethylene glycol, propylene glycol or 1,3- propanediol ester of (12) above; or

(17) any gum resin materials used as dispersing aids; or

(18) any wax ionomer or dispersing aid; or

(19) any sorbitan fatty ester; or

(20) any sorbitan polyoxyethylene ester; or

(21) any polyoxyethylene glycol (C_1 to C_{30}) ester; or

(22) any polymeric based hyper-dispersant; or

(23) any C_4-C_{40}, primary, secondary, tertiary or quaternary amine or salt thereof, or

any combination of (12) to (23) above.

In a preferred method, the plasticiser includes Triacetin. Glycerol mono-stearate as a stabiliser is also particularly useful. The stabiliser may also include a blend of stabilisers including a stearic acid salt and/or stearamide. Advantageously, the stabiliser comprises calcium stearate alone or in admixture with another stabiliser compound.

Mixing may be carried out at a temperature of at least 55°C to form a plasticised compound which can be thermoplastically processed at a temperature of at least 120°C.

The plasticiser or blend thereof is preferably used in an amount from 2-30% weight equivalents of the polymer or copolymer. The stabiliser or blends thereof is preferably used in an amount from 2-6% weight equivalents of the polymer or copolymer.

In addition to the above components, the mixture may include one or more of a) fillers including pigments and dyes, inorganic materials such as barium sulphate or calcium carbonate, or organic materials such as starch and b) conventional auxiliaries such as anti-oxidants and ultraviolet stabilisers.

The invention also provides a biodegradable article or material manufactured from a homogeneous biodegradable plastics compound prepared by mixing a polyhydroxylated polymer or copolymer with a plasticiser or a blend of plasticisers and a stabiliser or a blend of stabilisers, the stabiliser or blend thereof comprising a surface active agent, dispersing aid and/or mould lubricant and thermoplastically processing the mixture at 120°C to 205°C, the thermoplastic processing including compounding the mixture at a temperature in the range of 140°C to 205°C, the resulting compound having a melt flow index of 0.2 to 375 g/10 minutes using 21.6Kg at 190°C (ISO 1133 method), the plasticiser and stabiliser or blends thereof rendering the mixture stable to thermoplastic processing, with the proviso that the stabiliser does not comprise stearamide or stearic acid salt when used singly as the stabiliser at a mixing temperature of 106°C to 140°C with polyvinylalcohol or polyvinylalcohol/ polyvinylacetate copolymer.

<u>The Effects of Heat Energy on Plasticised PVA/PVAc</u>

Evidence of Chemical Degradation

Variable levels of thermal degradation can occur to PVA/PVAc copolymer, even when plasticised, depending upon the energy applied to the copolymer in the form of temperature, time exposed to temperature and mechanical energy applied during processing. The variable and erratic nature of these factors in conventional manufacturing have rendered these materials unpredictable in nature and difficult to use. Also, excessive degradation would alter the physical properties of the PVA plastics material, rendering it mechanically weaker (than non-degraded material), discoloured, and as a consequence of altering its chemical structure, also alter its bio-degradation properties.

Unplasticised PVA undergoes significant decomposition on melting rendering it impractical as a thermoplastic. Even plasticised PVA/PVAc may decompose by more than 5% when conventionally processed above 205°C. The degree of decomposition can be reduced to insignificant levels by working with plasticised and stabilised PVA/PVAc below 185°C, as indicated below.

Differential Scanning Calorimetery (DSC) studies of compounded plasticised PVA exposed to heat (Figure 1 shows exemplary DSC results, obtained using the material of Example 5 below) indicate that at temperatures close to 100°C the material looses free water. On subsequent heating to 170-185°C the material melts with loss of approximately 2-3% water of crystallisation. This water of crystallisation is rapidly re-absorbed from atmospheric moisture over 7-14 days post processing. On subsequent heating of the material to 185-200°C irreversible dehydration occurs and at temperatures above 200°C the material becomes discoloured. Rapid degradation commences from 205°C limiting the length of time for which the material can be worked at high temperature without compromising the material's chemical integrity and dissolution characteristics.

Thermal damage is evident by visible discoloration of the material (ie. it is rendered slightly amber / honey coloured). On examination of a 1% aqueous solution of the degraded material by UV, significant absorbance peaks at 280 and 340 nm are observed, and are attributable to -CH=CH-CH=CH- and -CH=CH-CH=CH-CH=CH- structures respectively which are created by dehydration. The IR spectrum of a thin film indicated a small band at 2,065cm^{-1}, attributed to the stretching frequency of the structure -C=C=O of damaged polymer end groups. The aforementioned discoloration and UV and IR absorbance are not evident in pure materials processed below 185°C.

Discoloration and evidence of unsaturation in UV and IR spectra of materials compounded above 185°C (as indicated above) increase in intensity with increase in compounding temperature over the range 190-220°C and slows thereafter. In addition, excessive energy applied to the compound and excessive time exposure to heat increase the visible signs of

decomposition. These observations are attributed to the creation of UV and IR absorbing moieties by dehydration and their subsequent destruction by cross-linking and pyrolysis.

In addition to the above, there is a change in the relative viscosity of material (of a 4%w/w aqueous colloidal solution at 20°C), indicative of intermolecular cross-linking in materials processed above 195°C. At temperatures above 240°C the material becomes so significantly degraded that its aqueous dissolution characteristics become compromised.

Biodegradation Properties of Thermoplastic Processed PVA/PVAc

Biodegradation of a material is definable as its breakdown by action of bacteria. As a measure of biodegradation of a test material we have used the following definition: The ratio, expressed as a percentage of the Biological Oxygen Demand over a 5 day period (BOD5), verses its Chemical Oxygen Demand (COD) of a 1% aqueous solution/colloidal suspension of test material. The BOD5 is a measure of bio-digestion by bacteria and the COD reflects the comparative amount of oxygen for the theoretical 100% digestion of the material. The BOD5 is critically determined on exposure to an unconditioned, broad spectrum bacteria effluent sludge, typical of municipal effluent water treatment. BOD5 and COD are expressed in mg/l Oxygen. BOD5 and COD measurements were determined by ALcontrol UK, (test methods 5.1.1 and 5.2.3; Test Method References; 'Methods for Examination of Waters and Associated Materials', HMSO 1988, ISBN 0-11-752212 0 and 'Chemical Oxygen Demand of Polluted Waste Waters', 1st Edition, HMSO, 1977, ISBN 0-11-751249-4). The aforementioned is regarded as a measure of the quantitative bio-digestion of a test sample by bacteria under conditions realistically modelling discharge to the environment.

Materials showing poor BOD5/COD may be judged an environmental hazard from the point of view of bio-accumulation (ie at risk of accumulating in the biosphere). Also, as many environmental agencies judge pollution discharge in surface water and ground water by COD measurement, the environmental discharge of non-degrading materials as soluble

COD or poorly degrading material, sometimes referred to as 'hard COD', may constitute a risk of breach of permitted environmental discharge limits.

Partly thermally degraded PVA will undergo dissolution in water, but mere dissolution is not biodegradation, and the ability of a material to dissolve may not be equated to true biodegradation, either immediately or in the long term. Uncompounded PVA/PVAc is biodegradable and exhibits a typical BOD5/COD ratio of 0.2 to1%. Thermally damaged materials (exhibiting visible, UV and IR spectroscopic evidence of degradation, indicated above) and some PVA copolymers exhibit BOD5/COD ratios of less than 0.2% and in some cases less than 0.1%, eg Economaty AX2000 exhibiting visible, UV and IR evidence of thermal degradation gave a BOD5/ COD ratio of <0.15%.

Plasticised PVA compound (10-15 weight % glycerol as plasticiser) exhibits improved biodegradability (BOD5/COD ratios 3-10%) due to decomposition of their plasticiser content and also by the consequential improved inoculation effect accelerating biodegradation of the PVA. As with unplasticised materials, materials exhibiting visible, UV and IR spectroscopic evidence of thermal degradation have lower BOD5/COD ratios indicative of poorer biodegradation qualities. Materials with comparable amounts of the same plasticiser can exhibit greatly differing BOD5/COD ratios based on their thermal treatment.

We have now found that thermoplastic compounding of plasticised PVA or PVA/PVAc below 185°C will retain the same BOD5/COD ratio of its plasticised compound prior to thermoplastic processing. Between 185 and 205°C the BOD5/COD ratio falls by 25-50% depending upon the stabiliser/plasticiser enhancer system employed. Above 205°C biodegradation properties as defined by the BOD5/COD ratio become increasingly compromised. Materials processed above 240°C become so degraded that their PVA content can be regarded as virtually non-biodegradable. In addition to the aforementioned, plasticised PVA compounds manufactured from PVA raw materials demonstrating visible, UV and IR evidence of unsaturation and potential thermal damage whether by dehydration or chemical inclusion or derivatisation of the polymer tend to exhibit poorer BOD5/COD

ratios post thermoplastic extrusion, indicating poorer thermal stability. In conclusion, the apparent retardation of biodegradation of PVA is disproportionate to the degree of chemical alteration of the material, ie a small amount of thermal degradation, severely slows digestion of the dissolved compound by bacteria.

The present invention provides an improved method for the manufacture of biodegradable plastic materials comprising mixing a biodegradable polymer, especially PVA/PVAc copolymer (70-95% PVA and 30-5% PVAc) with systems of 'plasticiser' and 'stabiliser' at temperatures from 55-150°C. Mixing is typically carried out in a force action blender or other conventional polymer mixing apparatus. The exact mixing temperatures reached have been found to be non-critical. The key parameters to efficiency of the plasticising process have been found to be mechanical efficiency, temperature and time in combination. Thus, high speed mixing of a compound previously made at a high temperature can be carried out at lower temperature with less vigorous mixing but would require a longer cycle time.

The action attributed to the stabiliser is to enhance the action of the plasticiser and maintain the stability of the resultant compound. The invention relates to the use of combinations of materials in the stabiliser system, which tends to magnify the system's effectiveness. The resultant material can be conventionally processed in numerous thermoplastic applications at temperatures of 120-205°C, eg; into blown film, sheet or other extrusion, injection moulded articles, woven or non-woven fibres or expanded foam products, or compounded as pellets for re-use in the aforementioned applications, and the resulting products have superior biodegradability characteristics, as measured by the BOD5/COD ratio, than have conventionally formulated and compounded PVA or PVA/PVAc products.

The materials produced by the present invention have improved melt flow characteristics as illustrated by their Melt Flow Index (MFI) whilst retaining good strength characteristics. and are therefore capable of being manipulated at lower temperatures than comparable materials previously disclosed, thereby incurring minimal or negligible thermal degradation. Therefore, the materials produced can be worked and re-worked with a

greater degree of control and reproducibility of physical performance in application and much less visible discolouring of the material, in particular in applications exhibiting minimal degradation from 205-185°C and in applications exhibiting negligible degradation from 185-120°C. Materials worked below 185°C so that irreversible degradation of the compound is avoided retain the positive biodegradation qualities of their PVA/PVAc starting materials. For example, the present invention renders the material capable of being worked at comparatively low pressures and temperatures of 40-75 bar (kN/m^2) at 120-185°C, with BOD5/COD ratio of 10.0%, whereas comparably plasticised PVA in the invention described in Irish Patent No. S71912 discloses typical pressures of 40-75 bar (kN/m^2) at temperatures of 200°C and exhibits a BOD5/COD ratio of 6.8%. Comparably plasticised but un-stabilised PVA compounded at 200°C exhibits a BOD5/COD ratio of 4.9%. Comparably plasticised commercially available PVA film eg. Aquafilm (Trademark) cold water and hot water soluble grades exhibit BOD5/COD ratios in the range 3.0-5.3%.

It has long been known that the degree of hydrolysis of PVA plays a role in improving MFI and processability of PVA/PVAc due to a process termed 'internal plasticisation'. Simply decreasing the hydrolysis level of PVA/PVAc polymers (ie. increasing PVAc content) will improve MFI at comparative temperature and pressure but produce brittle materials of little commercial worth. The present invention provides for materials whereby the molecular weight (MWt) of the polymer and the composition of the Plasticiser/Stabiliser system may be additionally varied to influence MFI in a predictable and controllable manner. Materials compounded according to the present invention exhibits a linear log / -log relationship between molecular weight and MFI, and the slope of this relationship is apparently the same for different plasticiser systems while the relationship constant varies between systems. Evidence for this effect is demonstrated in Figure 2, which plots the log molecular weight against the log of the melt flow index for different PVA plasticiser/stabiliser systems. Admix 1 in the figure comprises Stearamide: calcium stearate 2:1 and admix 2 comprises Glycerol monostearate: calcium stearate 2:1.

According to the method of the invention, it is possible to observe a correlation between MFI and the optimum die temperature at which we found we could produce a good quality film, as shown in Figure 3, which shows that there is a direct relationship between die extrusion temperature and log MFI. The results shown in Figure 3 were obtained using a Prism TSE 16TC twin screw extruder with a 90 degree, 30mm Blow Die operating at a barrel working temperature of 175-185°C and a pressure of 90 bar. Furthermore, we have found that the log MFI is directly correlated to the penetration performance on injection moulding under constant conditions, for which reference is made to Figure 4. The data shown in this figure were generated on a Demag S65 machine, using an injection pressure of 666 bar, a holding pressure of 450 bar, a back pressure of 100 bar, a cooling time of 10 sec, a holding time of 2 sec, a cycle time of 20 sec. and a barrel temperature of 180°C with a PVA/glycerol/admix 1 as described above.

We have also surprisingly found that the present invention also enables the achievement of enhanced fluidity of the melted plastic material than hetherto available by the use of amounts of stabiliser at 2-6% weight equivalents. Considering the proven relationship between MFI and optimum die operating temperature, Figure 5 gives an illustration of the use of levels of Stabiliser from 0-6%, demonstrating significant beneficial effect on lowering Die Temperature and ergo on improving MFI. The typical 'S' shape of the illustrations shown in Figure 5 indicate that the significant beneficial effect of relatively higher levels of Stabiliser (namely 2-6%) is not obtained at lower levels. This surprising effect is wholly unpredictable from applications of similar compounds used as mould lubricants at typically lower levels than 2%. At application levels above 5%, screw slip becomes evident and at levels above 6%, the beneficial effect is lost.

The plasticiser employed may be used in the range 2-30% weight equivalents. Plasticiser levels of 2-15% are generally preferred and the most preferred plasticisers are low-volatile liquids or low melting solids with a melting point of not greater than 100°C. As used herein, the term "low-volatile" refers to any material which is normally liquid at 20°C and 1 bar (1 MPa) and whose boiling point is greater than or equal to 150°C at 1 bar (1 MPa).

The process of the invention has the capability to produce a range of compounded plastic materials with varying physical characteristics, eg; melt flow index, strength, flexibility and rate of dissolution, depending upon the degree of hydrolysis of the PVA/PVAc copolymer, its average molecular weight and the qualities and type of Plasticiser(s) and Stabiliser(s) employed. The present invention includes the manufacture of such a range and its use in providing a plastics processor with materials which can be used alone or in any combination so that he may obtain materials to match his specific desired product performance criteria suitable for the manufacture of a wide variety of plastic articles with different performance needs, as exemplified in Table 1 below, which sets out observed technical data for a selection of the materials described in the examples below. Materials such as those whose manufacture is described herebelow, may be blended to give a material of predictable MFI and strength, providing an optimum in performance for a desired application between the two materials.

Thus, the present invention provides for the preparation of materials with varying properties which may be used predictably and reproducibly under real life production application conditions to manufacture multitudinous biodegradable products by conventional thermoplastic processes.

TABLE 1

TECHNICAL DATA

EXAMPLE	MFI 21.6Kg at 190°C (g/10 mins) ISO 1133	MFI 5.0Kg at 190°C (g/10 mins) ISO 1133	Spiral Mould Penetration 180°C&100bar (mm)	VICAT Softening Point at 1Kg (°C)	VICAT Softening Point at 5Kg (°C)	Strength of 30 micron thickness Film: Maximum Load (N) ISO 527	Strength of 30 micron thickness Film: Maximum Stress (MPa) ISO 527	Strength of 30 micron thickness Film: Elongation at Break (%) ISO 527	Shore Hardness D Scale ISO R868	COD 1% Colloidal Suspension g/IO	BOD5 1% Colloidal Suspension g/10	BOD5/COD Ratio %
9A	360	74	37	65	41	4	12	340	59	17-18	1.7-1.8	10.0
6A	265	35	34	74	40	6	17	230	71	16-17	0.8-0.9	7.0
5	30	4.3	20	67	36	8	30	250	64	17-18	1.7-1.8	10.0
6	19	2.8	16	82	40	12	50	100	75	16-17	1.1-1.2	7.0
7	6.5	2.5	13	89	47	14	70	65	81	16-17	0.8-0.9	5.2
8A	2.5	N/A	10	83	40	11	45	100	65	17-18	1.7-1.8	10.0
11E	50	20	34	65	35	5	12	195	75	18-19	1.5-1.6	8.4
11D	2	1.7	17	89	49	13	40	135	74	18-19	1.5-1.6	8.4

The 'Plasticiser' may be any material indicated in Schedule A or any combination of materials indicated in Schedule A.

The 'Stabiliser' may be any compound listed in Schedule B, (excluding stearamide or stearic acid salts when used on their own as sole stabiliser and the compound mixed at a temperature in the range of 106-140°C), or any combination of materials listed in Schedule B (including stearamide and stearic acid salts).

The materials listed in Schedules A and B hereunder are not limiting and other suitable materials or combinations of materials will suggest themselves to the skilled person.

All materials whose manufacture is described below are homogeneous compounds and may be conventionally blended with fillers, including pigments, dyes, barium sulphate, calcium carbonate or other inorganic materials, starch or other organic fillers and auxiliaries such as anti-oxidants and UV stabilisers. Materials with high surface polarity and or acidity or alkalinity such as silica, silicic acid, alumina and titanium dioxide should be avoided unless suitably deactivated by being rendered neutral or by coating such materials with an inert barrier such as mineral oils or silicone fluid.

Since the present invention discloses that PVA/PVAc polymers may be heat damaged, limiting their biodegradation, and describes how they may be manipulated thermoplastically with retention of their biodegradation properties by the super-plasticisation processes described herein, it follows that other co-compounds of PVA/PVAc with other polymeric materials or copolymers of PVA/PVAc with other monomers, eg ethylene, styrene, PET, PBT or other biodegradable monomers e.g. hydroxybutyrates, hydroxyvalerates or caprolactone, or indeed other poly-hydroxlayed polymers not related to PVA/PVAc may be similarly heat damaged with corresponding negative effects on biodegradation. All the aforementioned may be manipulated thermoplastically with stabilisation as described above to preserve their biodegradation properties using the super-plasticisation process of in the present invention.

The invention will now be described more particularly with reference to the following examples. Where references to materials are made by brand names, then the suppliers of those brands are listed either in the Example or in the Schedules.

Example 1

(Comparative Example)

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Glycerol - 15 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 125-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 170°C, 195°C and 170°C respectively. Working pressures were 60-95 bar (6-9.5 MPa). Pale yellow Pellet and film were obtained.

Example 2

(Comparative Example)

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Glycerol - 10 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 125-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die.

Temperatures at the feed-zone, work-zone and die zone were; 170°C, 200°C and 195°C respectively. Working pressures were 60-95 bar (6-9.5 MPa). Pale yellow Pellet and film were obtained.

Example 3

(Comparative Example)

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Glycerol - 5 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 125-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 170°C, 210°C and 210°C respectively. Working pressures were 60-95 bar (6-9.5 MPa). Pale yellow Pellet and film were obtained.

Example 4

(Comparative Example)

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Glycerol - 10 parts

Stearamide - 5 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 120-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 195°C and 170°C respectively. Working pressures were 60-95 bar (6-9.5 MPa). Good quality Pellet and film were obtained.

Example 4A

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Glycerol - 10 parts

Calcium stearate - 3 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 120-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 174°C, 186°C and 174°C respectively. Working pressures were 100 bar (10 MPa). Good quality Pellet and film were obtained.

Example 5

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Glycerol - 15 parts

Stearamide - 2 parts

Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 175°C and 140°C respectively. Working pressures were 40-75 bar (4-7.5 MPa). Good quality Pellet and film were obtained.

Differential scanning calorimetry results obtained with this material are shown in Figure 1.

Example 6

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Glycerol - 10 parts

Stearamide - 2.6 parts

Calcium Stearate - 1.3 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 195°C and 155°C respectively. Working pressures were 50-85 bar (5-8.5 MPa). Good quality Pellet and film were obtained.

Example 6A

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 20,000 - 100 parts

Glycerol - 10 parts

Stearamide - 2.6 parts

Calcium Stearate - 1.3 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 170°C and 135°C respectively. Working pressures were 50-70 bar (5-7 MPa). Good quality Pellet and film were obtained.

Example 7

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Glycerol - 5 parts

Stearamide - 3.33 parts

Calcium Stearate - 1.66 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 195°C and 170°C respectively. Working pressures were 50-85 bar (5-8.5 MPa). Good quality Pellet and film were obtained.

Example 8A

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 80,000 - 100 parts

Glycerol - 15 parts

Stearamide - 2 parts

Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 187°C and 159°C respectively. Working pressures were 65-95 bar (6.5-9.5 MPa). Good quality Pellet and film were obtained.

Example 8B

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 80,000 - 100 parts

Glycerol - 15 parts

Stearamide - 4 parts

Calcium Stearate - 2 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 153°C, 185°C and 153°C respectively. Working pressures were 55-90 bar (5.5-9 MPa). Good quality Pellet and film were obtained.

Example 9A

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 20,000 - 100 parts

Glycerol - 15 parts

Stearamide - 2 parts

Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 150°C, 165°C and 120°C respectively. Working pressures were 40-75 bar (4-7.5 MPa). Good quality Pellet and film were obtained.

Example 9B

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 20,000 - 100 parts

Glycerol - 15 parts

Stearamide - 2.7 parts

Calcium Stearate - 1.3 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 130°C, 174°C and 129°C respectively. Working pressures were 50-85 bar (5-8.5 MPa). Good quality Pellet and film were obtained.

Example 9C

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 20,000 - 100 parts

Glycerol - 15 parts

Stearamide - 3.3 parts

Calcium Stearate - 1.7 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 140°C, 172°C and 137°C respectively. Working pressures were 50-85 bar (5-8.5 MPa). Good quality Pellet and film were obtained.

Example 9D

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 20,000 - 100 parts

Glycerol - 15 parts

Stearamide - 1.3 parts

Calcium Stearate - 0.7 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 150°C, 170°C and 125°C respectively. Working pressures were 50-85 bar (5-8.5 MPa). Good quality Pellet and film were obtained.

Example 9E

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 20,000 - 100 parts

Glycerol - 2 parts

Stearamide - 2 parts

Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 100°C, 158°C and 144°C respectively. Working pressures were 45-65 bar (4.5-6.5 MPa). Good quality Pellet and film were obtained.

Example 9F

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 20,000 - 100 parts
Glycerol - 20 parts
Stearamide - 2 parts
Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 133°C, 145°C and 144°C respectively. Working pressures were 70-75 bar (7-7.5 MPa). Good quality Pellet and film were obtained.

Example 10

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Glycerol - 15 parts
Glycerol mono-stearate - 2 parts
Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 152°C, 178°C and 136°C respectively. Working pressures were 60-80 bar (6-8 MPa). Good quality Pellet and film were obtained.

Example 11A

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Glycerol - 12 parts
Triacetin - 3 parts
Stearamide - 2 parts
Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 152°C, 175°C and 129°C respectively. Working pressures were 60-80 bar (6-8 MPa). Good quality Pellet and film were obtained.

Example 11B

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Glycerol - 12 parts
Dioctyl adipate - 3 parts
Stearamide - 2 parts
Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 152°C, 183°C and 134°C respectively. Working pressures were 60-80 bar (6-8 MPa). Good quality Pellet and film were obtained.

Example 11C

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Triacetin - 15 parts

Stearamide - 2 parts

Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 155°C, 174°C and 160°C respectively. Working pressures were 60-80 bar (6-8 MPa). Good quality Pellet and film were obtained.

Example 11D

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts

Triacetin - 15 parts

Glycerol mono-stearate - 2 parts

Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-123°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 155°C, 174°C and 160°C respectively. Working pressures were 60-80 bar (6-8 MPa). Good quality Pellet and film were obtained.

Example 11E

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 20,000 - 100 parts

Triacetin - 15 parts

Glycerol mono-stearate - 2 parts

Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 170°C and 135°C respectively. Working pressures were 50-70 bar (5-7 MPa). Good quality Pellet and film were obtained.

Example 12

Ingredients:

PVA/PVAc (80-95%PVA:5-10%PVAc), Ave. MWt 40,000 - 100 parts

Glycerol - 10 parts

Stearamide - 2 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 120-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 170°C, 195°C and 185°C respectively. Working pressures were 65-95 bar (6.5-9.5 MPa). Slightly pale Pellet and film were obtained.

Example 13

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Glycerol - 15 parts
Solsperse 5000 - 3.0 parts
Calcium Stearate - 2.5 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 175°C and 140°C respectively. Working pressures were 65-70 bar (6.5-7.0 MPa). Good quality Pellet and film were obtained, but these were blue in colour owing to the inherent colour of Solsperse 5000.

Example 14

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Glycerol - 15 parts
Solsperse 28000 - 3.0 parts
Calcium Stearate - 2.5 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 175°C and 134°C respectively. Working pressures were 65-70 bar (6.5-7.0 MPa). Good quality Pellet and film were obtained.

Example 15

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Glycerol - 15 parts
Acylin 295A - 3.0 parts
Calcium Stearate - 2.0 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 175°C and 134°C respectively. Working pressures were 65-70 bar (6.5-7.0 MPa). Good quality Pellet and film were obtained.

Example 16

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Glycerol - 15 parts
Permalyn 5095 - 3.0 parts
Calcium Stearate - 2.0 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 175°C and 137°C respectively. Working pressures were 65-70 bar (6.5-7.0 MPa). Good quality Pellet and film were obtained.

Example 17

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Glycerol - 15 parts
Arquard HC Pastilles (Trade Mark of Akzo Nobel) (dimethyl-ditallow-ammonium chloride) - 3.0 parts
Calcium Stearate - 2.0 parts

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 160°C, 175°C and 146°C respectively. Working pressures were 65-70 bar (6.5-7.0 MPa). Good quality Pellet and film were obtained.

Example 18A

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Tributyl citrate butyric acid ester (B2 Jungbunzlaur) - 15 parts
Stearamide - 2 parts
Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 178°C, 183°C and 165°C respectively. Working pressures were 95-100 bar (9.5-10 MPa). Good quality Pellet and film were obtained.

Example 18B

Ingredients:

PVA/PVAc (75-80%PVA:25-20%PVAc), Ave. MWt 50,000 - 100 parts
Triethyl citrate (A1 Jungbunzlaur) - 15 parts
Stearamide - 2 parts
Calcium Stearate - 1 part

The Ingredients were combined and mixed in a force action blender between 1,500 and 3,000 rpm, until a temperature of 80-135°C was reached. The resultant powder was cooled to room temperature, sieved and compounded as pellet using a Prism TSE 16TC twin screw extruder with a 4.5mm die or Blown as film using 90°, 30 mm Blow die. Temperatures at the feed-zone, work-zone and die zone were; 183°C, 183°C and 159°C respectively. Working pressures were 95-10 bar (9.5-10 MPa). Good quality Pellet and film were obtained. (NB: excessive temperature on subsequent heat treatment can cause the plasticiser in this material to yellow significantly.

SCHEDULE A

(1) Glycerol, propylene glycol, 1,3-propanediol, ethylene glycol.

(2) Any mono-, di- or tri- (C_1 to C_{10}) carboxylic acid esters of materials listed (A1) above.

(3) citric acid (C_1 to C_4) alcohol tri-esters or mixed tri-esters or glycol esters or (C_1-C_4) acid esters thereof; or

(4) Tartaric acid (C_1 to C_4) alcohol di-esters or mixed di-esters or glycol esters.

(5) Lactic acid (C_1 to C_4) alcohol esters, ethylene or propylene glycol esters.

(6) Malic acid (C_1 to C_4) alcohol di-esters or mixed di-esters or glycol esters.

(7) Glyceric acid (C_1 to C_4) alcohol esters or ethylene glycol ester.

(8) Any (C_1 to C_4) ether, glycol ether or mixed ether of materials listed (A1) to (A7) above.

(9) Any (C_1 to C_4) acetal or ketal derivative of materials listed (A1) to (A7) above.

(10) Any vegetable base oils eg.; soya oil or corn oil.

(11) Any (C_1 to C_{10}) mono-, di- or tri- ester of adipic acid, azelaic acid, phthalic acid or trimellitic acid.

(12) Any combination of the above.

<u>SCHEDULE B</u>

(1) Any (C_4 to C_{36}) mono- or di-carboxylic acid

(2) Any primary, secondary or tertiary amide or diamide of (B1) above.

(3) Any inorganic or organic salt of (B1) above.

(4) Any mono-, di- or tri glycerol ester or mixed glycerol ester of (B1) above.

(5) Any ethylene glycol, propylene glycol or 1,3- propanediol ester of (B1) above

(6) Any gum resin materials used as dispersing aids, eg. Permalyn 5095 or 5110 (Trademark; Hercules Chemicals).

(7) Any wax ionomer or dispersing aid; eg. Aclyn 295A (Trademark; Allied Signal Inc).

(8) Any sorbitan fatty ester; eg. Span 20 to 85, (Trademark; Atlas Chemical Inc.) etc.

(9) Any sorbitan polyoxyethylene ester; eg Tween 20 to 85, (Trademark; Atlas Chemical Inc.) etc.

(10) Any polyoxyethylene glycol (C_1 to C_{30}) ester; eg Brij 30 to 96 (Trademark of Atlas Powder), etc.

(11) Any polymeric based hyper-dispersant; eg Solsperse 5000, 20000, 27000 or 28000 (Trademark of Zeneca), etc.

(12) Any C_4-C_{40}, primary, secondary, tertiary or quaternary amine or salt thereof.

(13) Any combination of the above.

It will of course be understood that the invention is not limited to the specific details described herein, which are given by way of example only, and that various modifications and alterations are possible within the scope of the invention as defined in the appended claims.

CLAIMS:

1. A method of manufacturing a homogeneous biodegradable plastics compound, comprising mixing a polyhydroxylated polymer or copolymer with a plasticiser or a blend of plasticisers and a stabiliser or a blend of stabilisers, the stabiliser or blend thereof comprising a surface active agent, dispersing aid and/or mould lubricant and thermoplastically processing the mixture at 120°C to 205°C, the thermoplastic processing including compounding the mixture at a temperature in the range of 140°C to 205°C, the resulting compound having a melt flow index of 0.2 to 375 g/10 minutes using 21.6Kg at 190°C (ISO 1133 method), the plasticiser and stabiliser or blends thereof rendering the mixture stable to thermoplastic processing, with the proviso that the stabiliser does not comprise stearamide or stearic acid salt when used singly as the stabiliser at a mixing temperature of 106°C to 140°C with polyvinylalcohol or polyvinylalcohol/ polyvinylacetate copolymer.

2. A method according to Claim 1, in which the compounding temperature is in the range of 140°C to 185°C and the biodegradability of the resulting compound is identical to that of the uncompounded mixture of its components.

3. A method according to Claim 1, in which the compounding temperature is in the range of 185°C to 205°C and the biodegradability of the resulting compound is reduced by not more than 30% of that of the uncompounded mixture of its components.

4. A method according to any of Claims 1 to 3, in which the polymer or copolymer comprises polyvinylalcohol or polyvinylalcohol/polyvinylacetate copolymer or a co-compound thereof.

5. A method according to claim 4, in which the co-compound is selected from polyethylene, polystyrene, polyhydroxy butyrate, polyhydroxyvalerate, polycaprolactone or any polyhydroxylated polymer or any thermoplastically processable polymer.

(21) any polyoxyethylene glycol (C_1 to C_{30}) ester; or

(22) any polymeric based hyper-dispersant; or

(23) any C_4-C_{40}, primary, secondary, tertiary or quaternary amine or salt thereof,

or any combination of (12) to (23) above.

10. A method according to any preceding claim, including the use of calcium stearate as the stabiliser, alone or in admixture.

11. A method according to any preceding claim, in which the plasticiser includes Triacetin.

12. A method according to any preceding claim, in which the stabiliser includes glycerol mono- stearate.

13. A method according to any preceding claim, in which the stabiliser comprises a blend of stabilisers including a stearic acid salt and/or stearamide.

14. A method according to any preceding claim, in which the mixing is carried out at a temperature of at least 55°C to form a plasticised compound.

15. A method according to any preceding claim, in which the plasticiser or blend thereof is used in an amount from 2-30% weight equivalents of the polymer or copolymer.

16. A method according to any preceding claim, in which the stabiliser or blends thereof is used in an amount from 2-6% weight equivalents of the polymer or copolymer.

17. A method according to any preceding claim, in which the mixture includes one or more of a) fillers including pigments and dyes, inorganic materials such as barium sulphate

or calcium carbonate, or organic materials such as starch and b) conventional auxiliaries such as anti-oxidants and ultraviolet stabilisers.

18. A biodegradable article or material manufactured by a method according to any preceding claim.

19. A biodegradable article or material manufactured from a homogeneous biodegradable plastics compound prepared by mixing a polyhydroxylated polymer or copolymer with a plasticiser or a blend of plasticisers and a stabiliser or a blend of stabilisers, the stabiliser or blend thereof comprising a surface active agent, dispersing aid and/or mould lubricant and thermoplastically processing the mixture at 120°C to 205°C, the thermoplastic processing including compounding the mixture at a temperature in the range of 140°C to 205°C, the resulting compound having a melt flow index of 0.2 to 375 g/10 minutes using 21.6Kg at 190°C (ISO 1133 method), the plasticiser and stabiliser or blends thereof rendering the mixture stable to thermoplastic processing, with the proviso that the stabiliser does not comprise stearamide or stearic acid salt when used singly as the stabiliser at a mixing temperature of 106°C to 140°C with polyvinylalcohol or polyvinylalcohol/ polyvinylacetate copolymer.

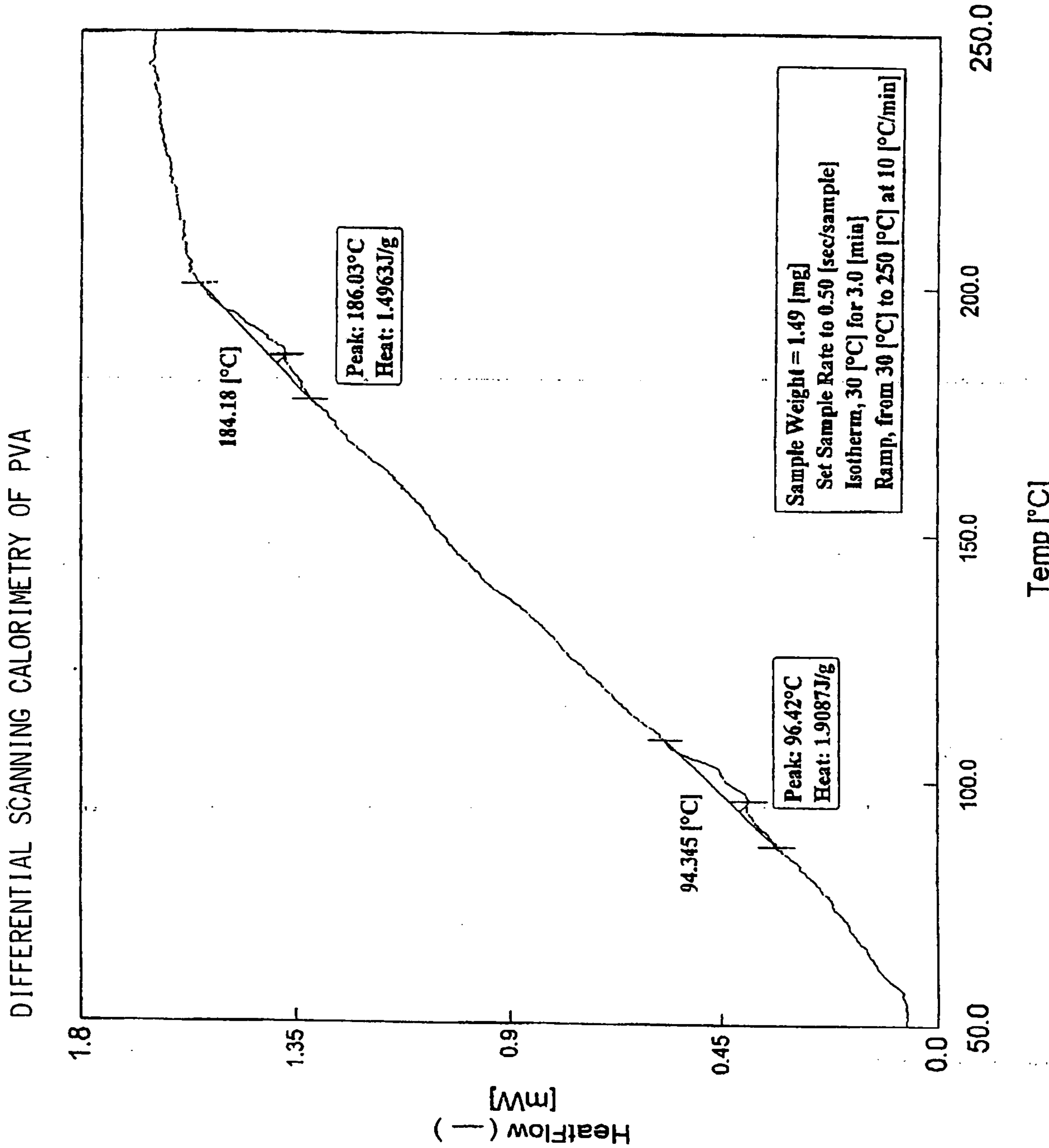
DIFFERENTIAL SCANNING CALORIMETRY OF PVA
HeatFlow (—)
[mW]
1.8
1.35
0.9
0.45
0.0
50.0
100.0
150.0
200.0
250.0
Temp [°C]
Peak: 186.03°C
Heat: 1.4963J/g
184.18 [°C]
Peak: 96.42°C
Heat: 1.9087J/g
94.345 [°C]
Sample Weight = 1.49 [mg]
Set Sample Rate to 0.50 [sec/sample]
Isotherm, 30 [°C] for 3.0 [min]
Ramp, from 30 [°C] to 250 [°C] at 10 [°C/min]

FIGURE 1

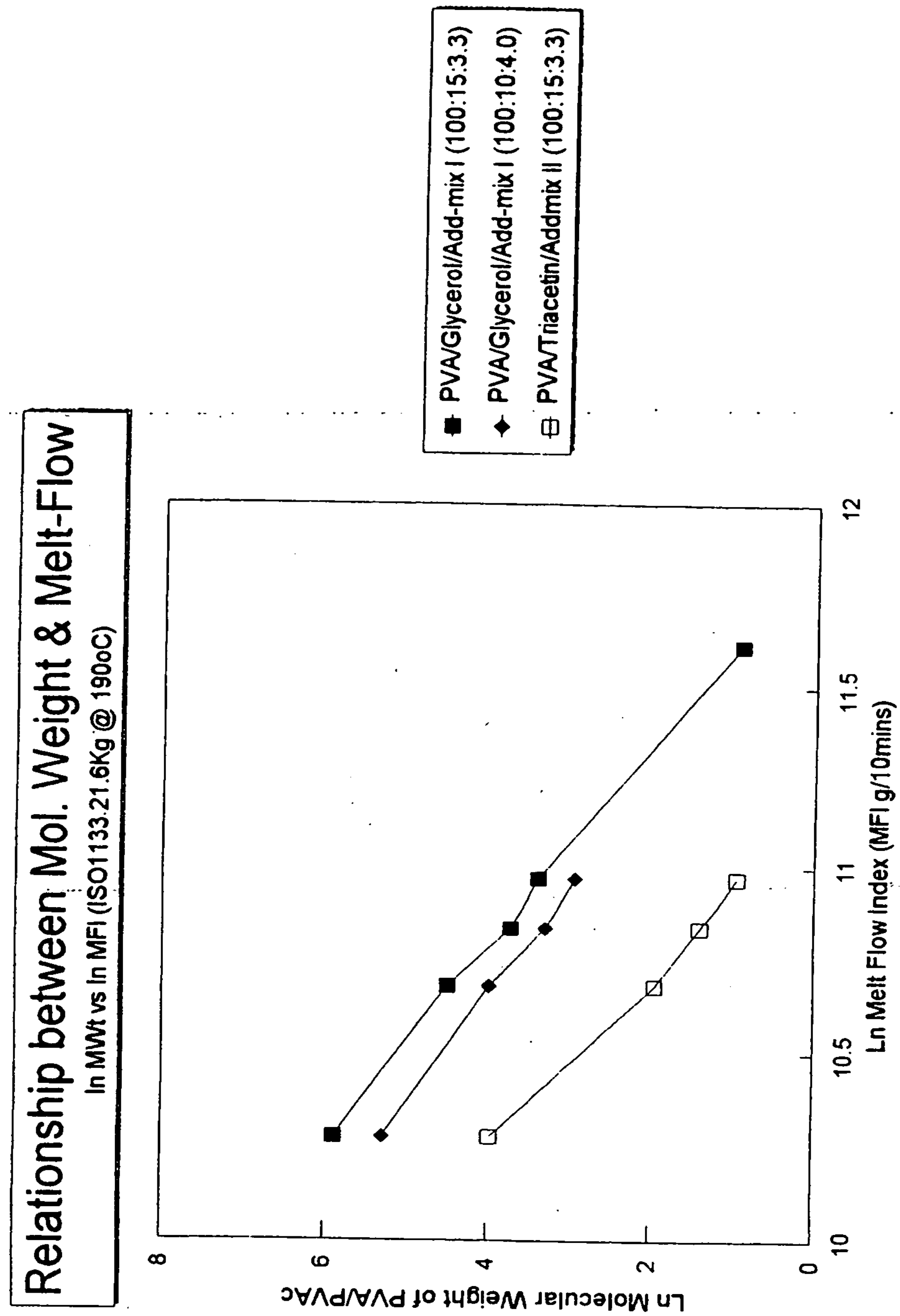
Relationship between Mol. Weight & Melt-Flow
ln MWt vs ln MFI (ISO1133.21.6Kg @ 190oC)
PVA/Glycerol/Add-mix I (100:15:3.3)
PVA/Glycerol/Add-mix I (100:10:4.0)
PVA/Triacetin/Addmix II (100:15:3.3)
Ln Molecular Weight of PVA/PVAc
Ln Melt Flow Index (MFI g/10mins)
0
2
4
6
8
10
10.5
11
11.5
12

FIGURE 2

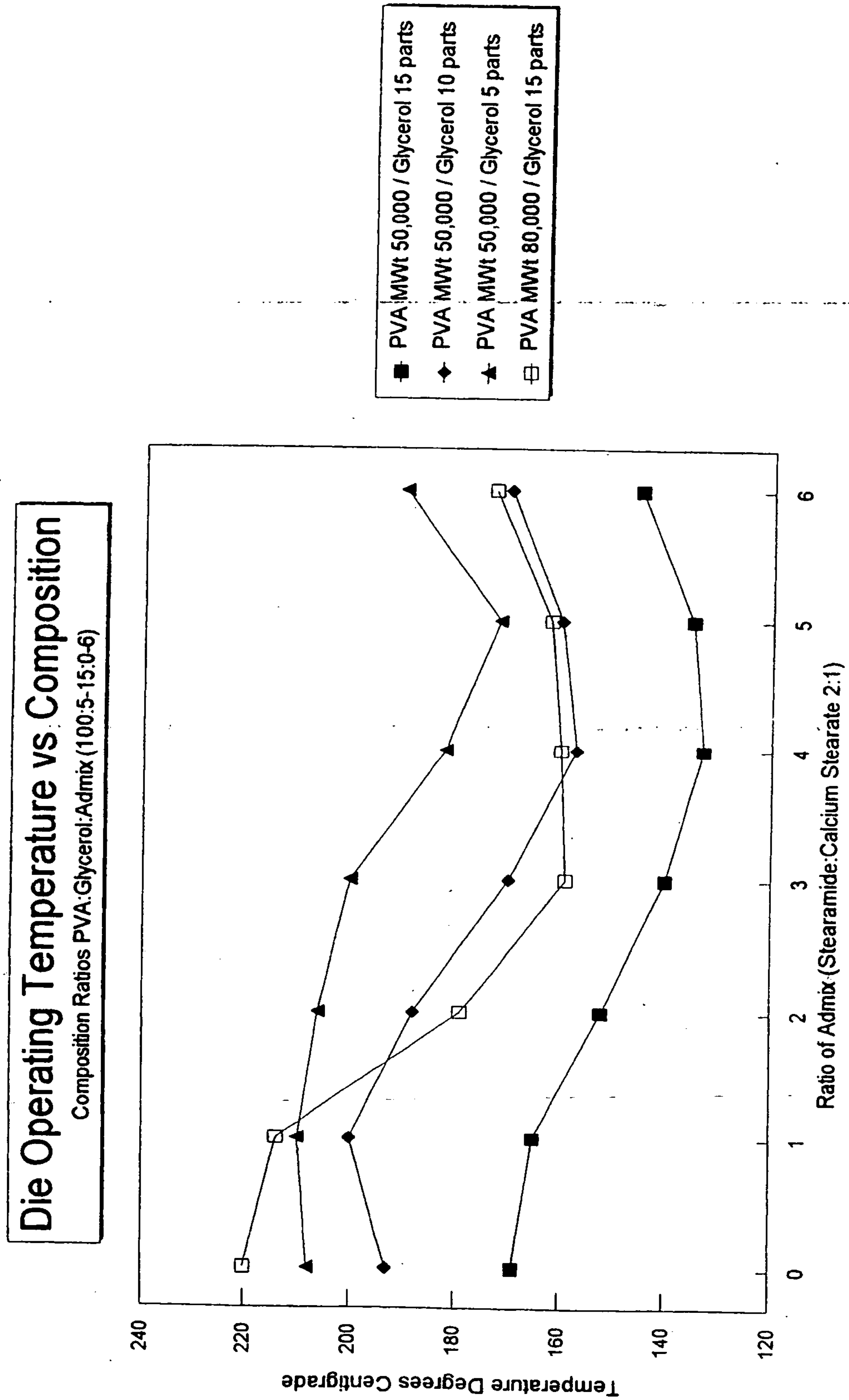
Die Operating Temperature vs Composition
Composition Ratios PVA:Glycerol:Admix (100:5-15:0-6)
PVA MWt 50,000 / Glycerol 15 parts
PVA MWt 50,000 / Glycerol 10 parts
PVA MWt 50,000 / Glycerol 5 parts
PVA MWt 80,000 / Glycerol 15 parts
Temperature Degrees Centigrade
240
220
200
180
160
140
120
0
1
2
3
4
5
6
Ratio of Admix (Stearamide:Calcium Stearate 2:1)

FIGURE 5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IE 98/00022

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K5/00 C08L29/04 C08J3/20 //(C08K5/00,5:053,5:06,
5:103,5:09,5:098,5:20)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K C08J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 724 388 A (NEGOCE ET DISTRIB. SA) 15 March 1996 see claims 1,2,11; example 1	1,4,8,9, 12,19
P,A	WO 97 09379 A (SOLPLAX LTD.) 13 March 1997 cited in the application see page 4, line 24 - page 5, line 20; claims 1,2,10,15,16,18; examples	1,4,8
A	US 3 997 489 A (COKER) 14 December 1976 cited in the application see examples 24,25,27.33; table II	1,8,9,12
A	US 3 607 812 A (TAKIGAWA ET AL.) 11 May 1971 see column 2, line 59 - column 3, line 9 see column 4; tables see claims 1,5,7	1,8,9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 July 1998	20/07/1998

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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